

Resonant X-ray Fluorescence Holography: Three-Dimensional Atomic Imaging in True Color

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X-ray fluorescence holography (XFH) is a relatively new experimental tool for directly determining the local three-dimensional atomic structure around a given type of atom [1-4]. This element-specific method is based on the same concept as photoelectron holography [5], but detects instead fluorescent x-ray photons.

In the first type of XFH to be demonstrated experimentally [1a], one measures the interference between the fluorescent radiation directly emitted by the excited atoms and additional wave components of the same radiation scattered by various near-neighbor atoms. It is thus necessary to measure a given fluorescent intensity as a function of the direction of emission over as large a solid angle as possible. This method, for which the fluorescent atoms inside the sample act as sources and the intensity is measured in the far field, has been termed normal x-ray fluorescence holography (XFH) [2] or more specifically “direct XFH”. In parallel with the first direct XFH experiment, Gog et al. [2a] proposed and demonstrated a different approach (termed multiple energy x-ray holography (MEXH) or “inverse XFH”) by applying the optical reciprocity principle and exchanging the roles of source and detector. In this case, the fluorescent atoms inside the sample become the detectors for the net field produced by the interference of the incident x-ray beam and the components of this beam that are scattered by near-neighbor atoms. With present detection systems, MEXH is faster, as the incident beam can be very intense (e.g. emitted directly from a beamline monochromator or an undulator harmonic), and one can furthermore in principle detect all of the fluorescence emitted above the sample surface. Here, one is thus measuring the total fluorescence yield of a given atomic transition as a function of the direction of the incident x-ray beam. Being able to measure at multiple energies also results in images with less aberration due to twin-image effects and other non-idealities [2,5,6]. Recent XFH/MEXH studies have demonstrated the ability to image a first-row element in the presence of a transition metal [3], and to study the local atomic environment in a quasicrystal, even though translational periodicity is lacking for such a system [4]. Current experiments are by and large detector-limited as to the speed of data acquisition. In the ALS Compendium of 2000, we have discussed a project that has successfully measured the first MEXH holograms and holographic atomic images at the ALS [7].

Even though XFH and MEXH in their current formulations offer powerful methods to probe the local atomic structure around a given atom, there still remains one deficiency: the techniques may be element-specific for the central fluorescing atom in the structure (a quality they share with extended x-ray absorption fine structure (EXAFS)), but there is no simple way to determine the

near-neighbor atomic identities. Use can be made of the differences in non-resonant x-ray scattering strengths between different atoms (as is done with differences in electron scattering strength in EXAFS), but this is only unambiguous when atomic numbers are relatively far apart, as recently illustrated for the case of O and Ni in NiO [3]. In the present work, we propose a significant improvement to MEXH, resonant x-ray fluorescence holography (RXFH), that should enable the direct discrimination of different atoms in reconstructed images, even for the most difficult cases where atomic numbers of elements involved are very close together. It is in this sense that we can finally speak of atomic images "in true color" [8].

The principle of RXFH is discussed here for the example of a binary compound of AB_3 type with close atomic numbers, specifically FeNi_3 , for which $Z_{\text{Ni}} - Z_{\text{Fe}} = 2$ and the fractional change in atomic number is only ~ 0.08 [8]. The central fluorescing atom of the reconstructed images is always chosen to be atom A (Fe in this case), and the anomalous dispersion associated with an absorption edge for element B (Ni in this case) is used to selectively image atoms B surrounding the central atom. In the usual implementations of MEXH in which both atoms A and B are to be equally imaged, the incident x-ray energies E are usually chosen in such a way that they are close enough to E_{abs}^A , the absorption edge of element A , for the efficient excitation of fluorescent x-rays from A , but also far enough from both E_{abs}^A and any edges E_{abs}^B of atom B that the anomalous dispersion terms in the x-ray scattering factors for A and B are not significant. In RXFH, by contrast, we will choose several E 's in the vicinity of an absorption edge E_{abs}^B of element B . The basic idea here is thus similar to that of multiple-wavelength anomalous diffraction (MAD) for phase determinations in conventional x-ray diffraction studies, but with the significant difference that there is from the outset no phase uncertainty in MEXH.

Making use of experimentally determined x-ray scattering factors for Fe (non-resonant) and Ni (resonant), as shown in Fig. 1, we have thus theoretically simulated holograms [6b] for a large cluster of atoms representing the FeNi_3 lattice as the Fe $K\alpha$ fluorescence at 6.4 keV is monitored while scanning through the Ni K edge at about 8.3 keV [8]. As a first trial set of data, we have finally obtained MEXH and RXFH images based on the three energies shown in Fig. 2: below, on, and above the Ni K edge. One promising procedure for imaging in RXFH is shown elsewhere [8] to be using two difference holograms for E_1 - E_2 and (with reversed sign) E_3 - E_2 . Fig. 2 shows the FeNi_3 crystal structure, together with normal MEXH images and RXFH images from these difference holograms. Fig. 2 makes it clear that the Ni-atom images are strongly suppressed in the RXFH images, thus suggesting this as a new approach in x-ray fluorescence holography for identifying near-neighbor atoms to a given type of fluorescent emitter.

In conclusion, resonant x-ray fluorescence holography should make it possible to obtain additional information on near-neighbor chemical identities that would lead to a much more complete structural characterization of any system, particularly one in which possible compositional disorder on the nm scale is present, and thus to a much broader applicability for nanoscale materials characterization. Future experiments at the ALS will explore this approach experimentally.

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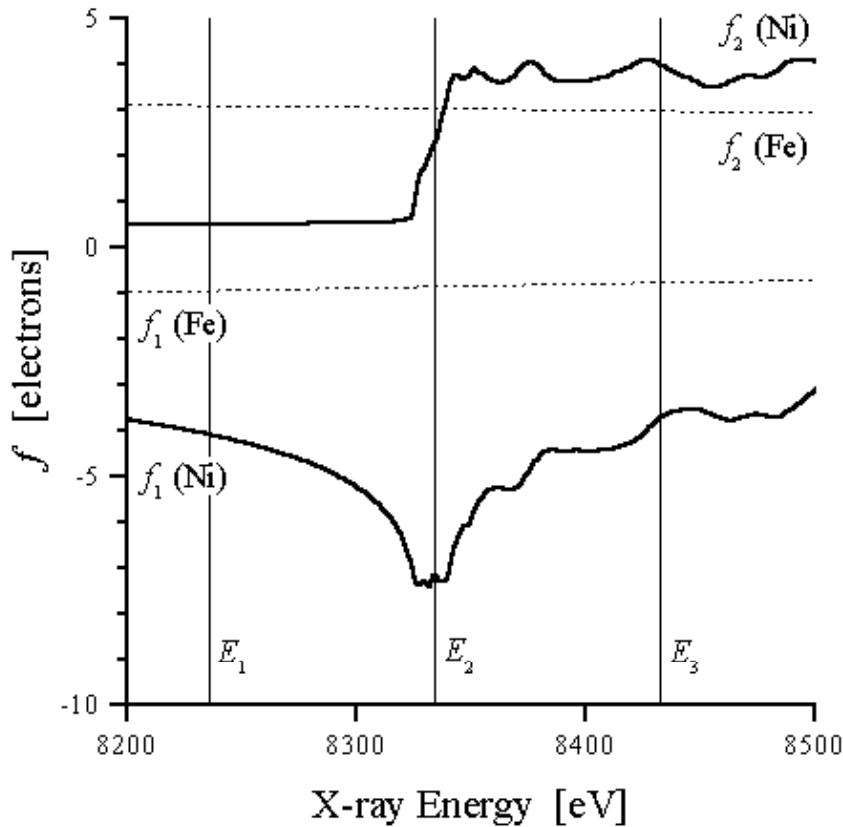


Fig. 1-- The atomic x-ray scattering factors f_1 and f_2 for Fe (dotted lines) and Ni (solid lines) as a function of x-ray energy around the K edge of Ni. The overall scattering factor is given by $f_{Atom} = f_0(\theta) + f_1 - if_2$, with $f_0(\theta)$ the form factor. The three energies used for the simulations of E_1 , E_2 and E_3 are indicated by vertical solid lines and correspond to 8235 eV, 8334 eV, and 8433 eV, respectively.

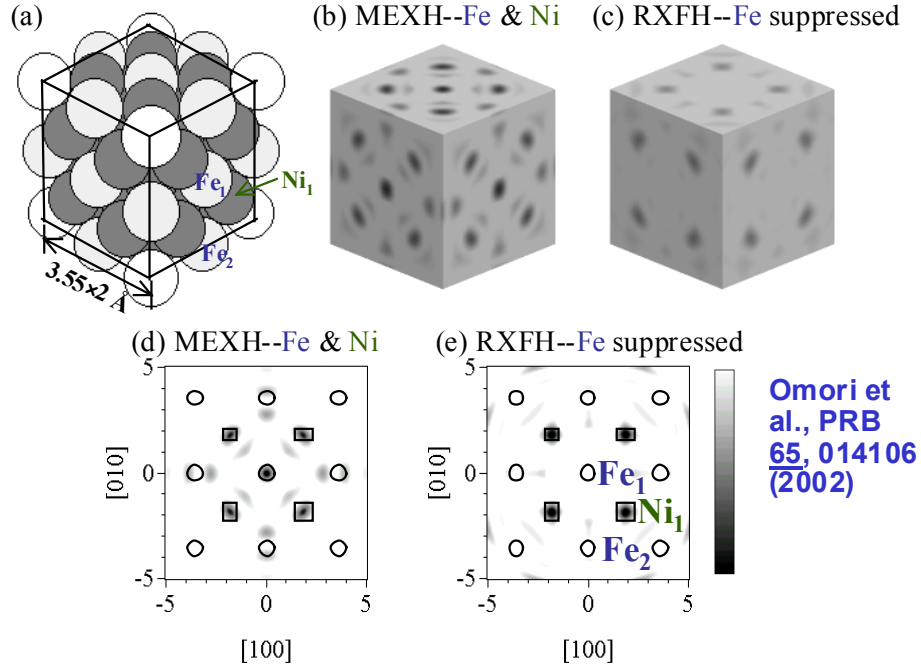


Fig. 2-- Comparison of multi-energy inverse x-ray fluorescence holographic images based on the negative of the real part of images generated using both the standard inversion algorithm (MEXH) and resonant holography (RXFH) based on two difference images (E_1-E_2 and E_3-E_2). These images are based on single-scattering cluster simulations of holograms [6b] at the three energies E_1 , E_2 and E_3 for an FeNi₃ crystal containing about 10,000 atoms. (a) Near-neighbor atomic model of FeNi₃ for comparison to the reconstructed images in (b) and (c) and including 8 unit cells with the lattice constant of 3.55 Å. Fe atoms are lighter gray, and Ni atoms darker gray. The unique types of Fe and Ni atoms observed in (b) are labelled as Fe₁, Fe₂ and Ni₁. (b) Three dimensional reconstructed image from MEXH in cross section along six {001} planes. (c) Corresponding image from RXFH. The fluorescing Fe atom is located at the centers of the cubes in (a), (b) and (c). (d) Enlarged reconstructed image from MEXH in the (001) plane. (e) Corresponding enlarged image from RXFH. The true atomic positions of Fe and Ni atoms are shown as circles and squares, respectively, and certain key atomic positions are also labelled.